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Possible mixed valence behavior of CeIr_2Ga and YbIr_2Ga

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Abstract

We report possible mixed valence behavior in the new ternary compounds CeIr_2Ga and YbIr_2Ga . These materials crystallize in the hexagonal Na_3As structure of space group $\text{P6}_3\text{cm}$. Magnetization, specific heat and transport measurements show reduced magnetic moments and the absence of magnetic order above 0.04 K. The quasi-2D structure of these compounds offers the possibility for investigating the role of spatial dimensionality on mixed valence phenomena. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The physics of lanthanide compounds is governed by the energy difference between localized 4f levels and the Fermi energy. For most lanthanides, the 4f level is sufficiently below the Fermi energy that they present a stable valence configuration. On the other hand, in mixed valence compounds the 4f level is near the Fermi energy causing charge and associated spin fluctuations among 4f and conduction-band electrons. Because of the low temperature energetic advantages of an empty (Ce^{4+}) or full (Yb^{2+}) 4f shell, compounds of Ce

and Yb are commonly mixed valent. Here, we present preliminary results on the thermal, magnetic and transport properties of CeIr_2Ga and YbIr_2Ga , which crystallize in the triple Na_3As structure of hexagonal space group $\text{P6}_3\text{cm}$ [1]. These new compounds offer an interesting possibility to investigate mixed valence phenomenon in a layered material. Neither material orders magnetically down to the lowest measured temperatures, implying substantial d–f hybridization.

2. Experimental techniques

Single crystals of CeIr_2Ga and YbIr_2Ga were grown from Ga flux with an initial composition of constituent elements Ce(Yb), Ir and Ga in the

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ratios of 1:1:20. The elements were placed in alumina crucible and sealed in a quartz ampoule in vacuum. The ampoule was heated to 1175°C, and then cooled to 300°C (500°C) in case of Ce (Yb) over a period of 175 (84) h, at which point the Ga flux was removed by spinning the ampoule in a centrifuge. For CeIr₂Ga the initial composition of the melt was varied between 1:1:20 and 1:2:20 atomic ratio. It was found that the diffraction patterns of crystals with starting a composition containing excess Ir showed extra peaks that could not be indexed on the Na₃As structure type [1,2]. Melt spinning at lower temperatures gave larger resistivity ratios $\rho(300\text{ K})/\rho(4\text{ K})$ and cleaner X-ray patterns with few additional Ga and/or Ce peaks due to secondary phases of residual flux. Additionally, CeIr₂Ga samples spun at different temperatures were annealed for one week at 650°C. The annealing of the crystals led to appearance of Ir peaks in the diffraction pattern, suggesting crystal degradation.

From X-ray powder diffraction data, we have concluded that the samples crystallize in the triple Na₃As hexagonal structure, space group P6₃cm [1,2]. The materials crystallized as large hexagonal rods up to 1 cm in length, a few millimeters in diameter. Their lattice constants were calculated from the peak positions using a least square method, with Si as the internal standard. Lattice constants and unit-cell volumes at the room temperature are $a_0 = 7.615\text{ Å}$, $c_0 = 9.528\text{ Å}$, $V = 478\text{ Å}^3$ for CeIr₂Ga and $a_0 = 7.490\text{ Å}$, $c_0 = 9.408\text{ Å}$, $V = 457\text{ Å}^3$ for YbIr₂Ga. The unit-cell volumes for CeIr₂Ga (YbIr₂Ga) are smaller (larger) than expected from the lanthanide contraction across the RIr₂Ga series [2]. These deviations are consistent with an admixture of Ce³⁺/Ce⁴⁺ and Yb³⁺/Yb²⁺ configurations in CeIr₂Ga and YbIr₂Ga, respectively. Additional X-ray powder diffraction spectra for CeIr₂Ga were taken at 200 K, 100 K and 15 K. Examination of the lattice parameters showed ordinary lattice contraction as the temperature is lowered with no structural phase transitions (Fig. 1. inset). CeIr₂Ga and YbIr₂Ga crystallize in the triple Na₃As structure model, as do all other members of the RIr₂Ga series [2]. Their layered quasi-2D structure consists of Ce(Yb)–Ga layers with hexagonal symmetry

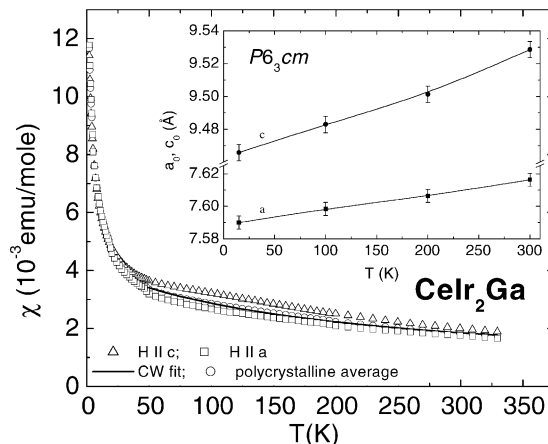


Fig. 1. Magnetic susceptibility of CeIr₂Ga as a function of temperature for a magnetic field applied along the *c*-axis (open triangles) and in the basal plane (open squares). A Curie–Weiss fit (solid curve) to a polycrystalline average of these data (open circles) is also shown. Inset: Lattice constants of CeIr₂Ga as a function of temperature.

that are separated by Ir layers stacked along the *c*-axis.

The electrical resistivity of samples was measured along their *c*-axis using a standard four-probe method. Samples selected for resistivity measurement were rather large hexagonal rods with a clearly defined *c*-axis. Magnetization measurements were made in a Quantum Design SQUID magnetometer in the temperature range $2\text{ K} < T < 350\text{ K}$. Specific heat was measured by the adiabatic heat-pulse technique in the temperature interval $40\text{ mK} < T < 20\text{ K}$. Hall effect experiments were performed in a conventional Hall geometry with a magnetic field applied perpendicular to the *c*-axis.

CeIr₂Ga has been studied in more detail than YbIr₂Ga. Considerable effort was made to obtain high-quality single crystals and to extract their intrinsic properties. Systematic studies suggest that CeIr₂Ga is stress sensitive. While the bulk properties of the material are not affected by mechanical polishing (magnetic susceptibility curves are the same for polished and unpolished samples), the resistivity below 25 K of polished rods showed a rise characteristic of disordered systems. All data shown, except for the specific heat and Hall constant, were taken on unpolished samples. For

both polished and unpolished samples, larger resistivity ratios were found for samples grown at slower cooling rates and lower spinning temperatures.

3. Results

The magnetic susceptibility of CeIr_2Ga is shown in Fig. 1 for measurements taken with a field $H = 0.1$ kOe applied parallel (χ_{\parallel}) and perpendicular (χ_{\perp}) to its c -axis. Values for the high temperature effective magnetic moment μ_{eff} and anisotropic Weiss temperatures θ_{\parallel} and θ_{\perp} were obtained from fits to the Curie–Weiss law (CW). The polycrystalline average of the magnetic susceptibility was calculated from $\chi_p = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$. In the temperature interval 100–350 K, χ_p could be fit to the modified Curie–Weiss law $\chi = \chi_0 + C/(T - \theta_p)$, which gives $\chi_0 = 1.4 \times 10^{-6}$ emu/g, $\theta_p = -120$ K and high temperature Ce moment $\mu_{\text{eff}} = (1.85 \pm 0.25) \mu_B$, with the relative error in parameter values of 14%. The value of μ_{eff} is reduced relative to the Hund's rule free ion value for Ce^{3+} of $2.54 \mu_B$. Since the effective moment is reduced from the expected value of $2.54 \mu_B$, the presence of some admixture of Ce^{4+} is likely ($\mu_{\text{eff}}(\text{Ce}^{4+}) = 0$ for empty 4f shell). Close inspection of the c -axis susceptibility reveals a shoulder near 100 K that can be viewed as a weak maximum below which χ rapidly increases. The large negative θ_p implies strong hybridization of Ce 4f electrons with the conduction band. The low-temperature susceptibility shows no sign of magnetic ordering down to 1.8 K. Anisotropic Weiss temperatures obtained were $\theta_{\perp} = -106$ K and $\theta_{\parallel} = -148$ K. Magnetic susceptibility for applied fields of 0.1 and 5 kOe show no signs of saturation, suggesting that the low- T upturn below 40 K in χ is largely intrinsic.

Anisotropic magnetic susceptibility data taken in $H = 0.1$ kOe for YbIr_2Ga are given in Fig. 2. $\chi(T)$ does not exhibit well-defined Curie–Weiss behavior up to 350 K. The susceptibility curves go through a broad maximum around 180 K (H parallel to the c -axis) or ~ 250 K (H perpendicular to the c -axis). This indicates even stronger hybridization effects that partially quench the Yb^{3+} moment even near room temperature. The YbIr_2Ga magnetic susceptibility and unit-cell

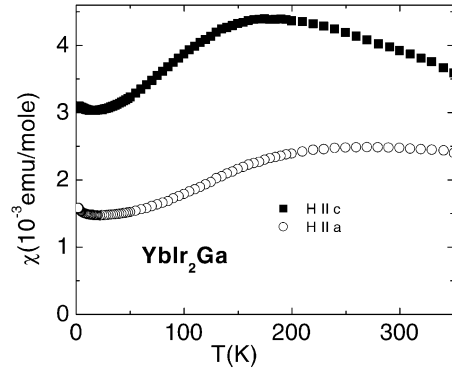


Fig. 2. Magnetic susceptibility of YbIr_2Ga as a function of temperature for a magnetic field applied along c -axis (full squares) and in the basal plane (open circles).

volume undoubtedly classify this compound as strongly mixed valent.

The specific heat divided by temperature C/T for CeIr_2Ga is plotted in Fig. 3(a), together with the magnetic contribution estimated by subtracting the specific heat of non-magnetic LaIr_2Ga . Above 5 K, C/T is nearly constant at a value around 0.08 J/mol K^2 but increases substantially below about 0.5 K. Entropy associated with this rise is small, roughly $0.04R \ln 2$. We will return to this observation in the discussion. The inset in Fig. 3(a) shows a fit to the relation $C/T = \gamma + \beta T^2$, from which we obtain $\gamma = 77.3 \times (2) \text{ mJ/mol K}^2$ and $\beta = 0.14(3) \text{ mJ/mol K}^4$ ($\theta_D = 383$ K). The specific heat for YbIr_2Ga is shown in Fig. 3(b) together with its magnetic contribution, estimated again by subtracting the specific heat of LaIr_2Ga . Fitting the data to $C/T = \gamma + \beta T^2$ (Fig. 3(b) inset) yields values for the electronic and phonon contributions to the specific heat of $\gamma = 21.7(2) \text{ mJ/mol K}^2$, $\beta = 0.700(4) \text{ mJ/mol K}^4$ ($\theta_D = 223$ K).

Resistivity data for CeIr_2Ga and YbIr_2Ga are shown in Fig. 4. The YbIr_2Ga resistivity is featureless, with a quadratic temperature dependence below 40 K, while CeIr_2Ga shows well-defined peak near 80 K. Below 40 K, the resistivity of CeIr_2Ga is described by $\rho = (170.1 + 0.042T^2) \mu\Omega \text{ cm}$. For YbIr_2Ga a fit to $\rho = \rho_0 + AT^2$ gives $\rho_0 = 76 \mu\Omega \text{ cm}$ and $A = 0.01 \mu\Omega \text{ cm K}^{-2}$.

The Hall coefficient R_H for CeIr_2Ga as a function of temperature is shown in Fig. 5. R_H is

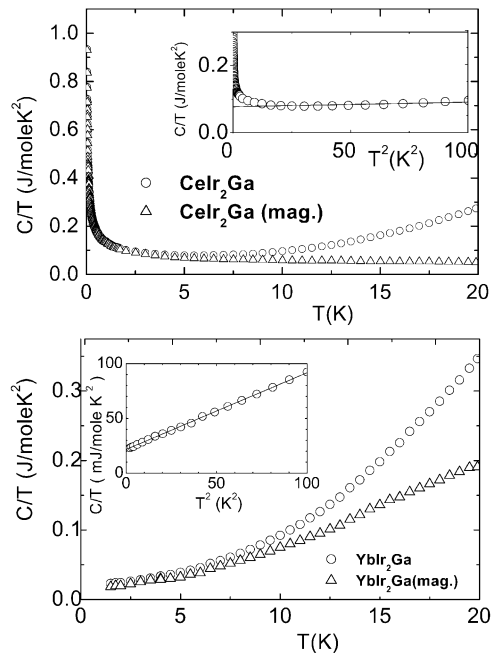


Fig. 3. (a) Specific heat divided by temperature for CeIr₂Ga as a function of temperature (open circles) and its magnetic contribution (open triangles). (b) Specific heat divided by temperature of YbIr₂Ga as a function of temperature (open circles) and its magnetic contribution (open triangles).

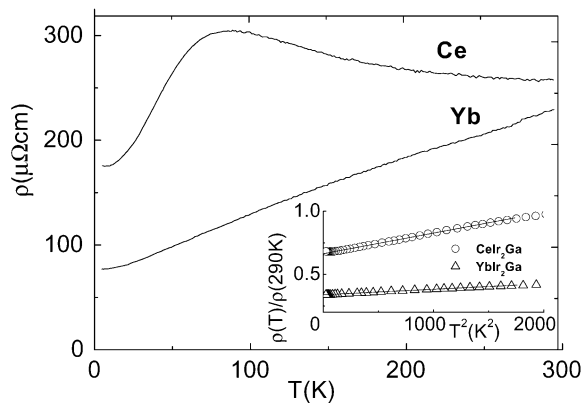


Fig. 4. Electrical resistivity of CeIr₂Ga and YbIr₂Ga as a function of temperature. Inset: Low temperature electrical resistivity as a function of T^2 for CeIr₂Ga (open squares) and YbIr₂Ga (open triangles).

weakly temperature dependent down to 100 K, below which it increases by over an order of magnitude.

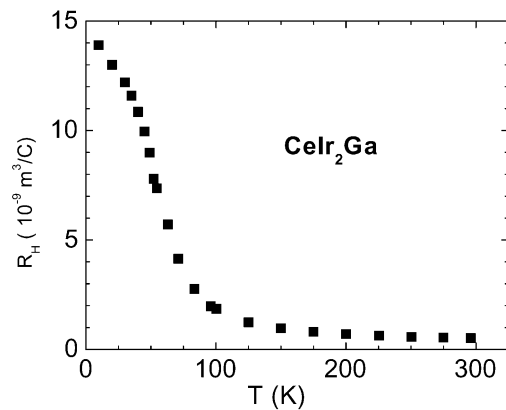


Fig. 5. Hall constant of CeIr₂Ga as a function of temperature.

4. Discussion

In materials that are mixed valent, several characteristic signatures are usually apparent [4]. The unit-cell volume differs from that expected of strictly trivalent rare-earth isomorphs; the magnetic susceptibility exhibits a maximum at a temperature proportional to the spin (valence) fluctuation temperature; and there is an enhanced electronic contribution to the heat capacity. Additionally, a T^2 contribution to the low-temperature resistivity is observed whose magnitude is proportional to the enhancement of the electronic specific heat. As shown in Section 3, all of these properties are observed in CeIr₂Ga and YbIr₂Ga. In such cases, a characteristic spin-fluctuation temperature can be inferred from, for example, the Coqblin–Schrieffer model for an orbitally degenerate Kondo-impurity system [3].

Although the values of γ are not particularly large, both CeIr₂Ga and YbIr₂Ga display an enhanced electronic specific heat relative to typical values found in normal metals ($\sim 1\text{--}10 \text{ mJ/mol K}^2$) consistent with mixed valence behavior. Rajan's solution to Coqblin–Schrieffer model [3] predicts $\gamma = (v-1)\pi k_B/6T_0$, where v is the degeneracy and T_0 is the characteristic spin-fluctuation temperature. Taking the measured values of γ for CeIr₂Ga and YbIr₂Ga and assuming full orbital degeneracy for the Ce³⁺ and Yb³⁺ ions ($v = 6$ and 8, respectively), we find $T_0 \sim 280 \text{ K}$ and 1380 K for

CeIr₂Ga and YbIr₂Ga, respectively. This same model predicts a maximum in $\chi(T)$ at a temperature of approximately $(0.3\text{--}0.5) T_0$ for $J > \frac{1}{2}$. From the results of Figs. 1 and 2 discussed above, we estimate $T_0 \sim 200\text{--}300$ K for CeIr₂Ga and $\sim 600\text{--}900$ K for YbIr₂Ga, which agree qualitatively with estimates from specific heat measurements. An additional test of this characterization is the self-consistency of the proportionality between γ and the T^2 coefficient of ρ . Kadowaki and Woods [5] have shown that the ratio $A/\gamma^2 \sim 10^{-5} \mu\Omega \text{ cm}(\text{mol K/mJ})^2$ is common to several heavy-fermion and mixed valence compounds. CeIr₂Ga seems to follow this ratio since $A/\gamma^2 = 0.7 \times 10^{-5} \mu\Omega \text{ cm}(\text{mol K/mJ})^2$. A somewhat enhanced value is obtained for YbIr₂Ga, $A/\gamma^2 = 2 \times 10^{-5} \mu\Omega \text{ cm}(\text{mol K/mJ})^2$. Thus, CeIr₂Ga (at relatively high temperatures) and YbIr₂Ga seem to be fairly typical mixed valence materials with characteristic temperatures of $\sim 200\text{--}300$ K and $\sim 1000 \pm 300$ K, respectively.

One final issue to discuss is the rise in susceptibility of CeIr₂Ga below 40 K and the specific heat increase at low temperatures. Susceptibility measurements at low temperatures are often influenced by an impurity contribution. This seems to be the case for YbIr₂Ga. In Fig. 3, we have shown data for a sample with the smallest ‘impurity tail’, but several other samples were measured with larger impurity tails. On the other hand, there was little or no difference in the low temperature increase of $\chi(T)$ among several CeIr₂Ga samples grown under different conditions. An applied field of 5 kOe also did not saturate the susceptibility below 40 K. Therefore, we conclude that the susceptibility of CeIr₂Ga at low temperatures appears to be intrinsic. We suggest that this intrinsic increase in $\chi(T)$ also may be related to the large increase in C/T at low temperatures. Unfortunately, a direct comparison between these two quantities is complicated by the substantial Ir nuclear-quadrupole moment contribution to C/T that is expected to develop on the temperature scale of a few tenths of a Kelvin. However, we note that, unlike the case of YbIr₂Ga, C/T is already beginning to increase below about 3 K in CeIr₂Ga (inset Fig. 3(a)), well above the temperature scale for a nuclear contribution. Together, these data suggest that there

might be a second low energy scale in CeIr₂Ga that deserves further investigation.

5. Conclusion

In summary, CeIr₂Ga and YbIr₂Ga are new intermetallic compounds that crystallize in the triple hexagonal Na₃As — type structure. Their properties indicate mixed valent behavior of the rare-earth ions and possibly the appearance of a second low-energy scale in CeIr₂Ga. Their crystal-line structure can be described as quasi-2D, where rare-earth dominated clusters and ligand clusters alternate along the *c*-axis. Among Ce- and Yb-based intermetallics, it is rather uncommon to find mixed valence behavior in systems having lower than cubic symmetry. These materials offer an interesting new example of mixed valence in a reduced dimensionality lattice where anisotropy may influence the screening of magnetic ions, the effective *f*–*d* interaction, and delocalization of 4*f* electrons. Substitutional studies in the magnetic-ion layers and ligand-Ir layers could offer interesting insight into the role of spatial dimensionality in the absence of magnetism and the formation of a mixed valent state.

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